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The Role of Chemometrics in Single and Sequential Extraction Assays. A Review. Part I. Extraction Procedures, Uni- and Bivariate Techniques and Multivariate Variable Reduction Techniques for Pattern Recognition

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Abstract

Element mobility and availability in natural solid matrices can be studied with single and sequential extraction procedures; such procedures provide reliable and useful information only if the experiments are correctly planned and executed and the results are properly interpreted.

Chemometrics can be a valuable tool for these aims, especially taking into account the large amounts of data generated with extraction essays and the complexity of the processes under investigation. This review deals with the application of chemometrics in research studies involving single and sequential extractions on soils or sediments, for several purposes: the development and optimization of the extraction conditions, the calculation of element fractionation, the visual illustration of the experimental results, the acquisition of different areas of information, including relationships among variables, similarities and differences among samples, causes of the observed behaviour (e.g. source identification), risk assessment, models and predictions of future events. In Part I of the review, following an overview on extraction procedures, the applications of univariate and bivariate chemometric methods are reported; then the principles of multivariate techniques for pattern recognition based on variable reduction, their applications and the main findings obtained are addressed.

Keywords: single extraction; sequential extraction; chemometrics; multivariate statistics; soil;

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sediment

1. Introduction

Single and sequential extraction procedures are widely used for the investigation of solid matrices, such as soil, sediment, sludge, fly ash and atmospheric particulate matter [1-4]. They provide information on the mobility and availability of metals and other elements, meanwhile identifying their potential negative impact through their release into other environmental compartments and entry into the food chain.

Mobility and availability depend on the reactivity and on the binding behaviour of elements with the components of the matrix, and cannot be assessed only from the values of the total concentrations. Single extractions may be used for estimating the most potentially mobile element fraction and/or, in the case of soils, the proportion amenable for plant uptake. A single extracting reagent (normally a ligand, diluted acid or salt) is used to treat the sample and measurement is made on the amount of elements released from the matrix of interest [2-3]. A more detailed overview on the properties and behaviour of the elements under investigation may be achieved through the utilization of sequential extractions. Reagents with different chemical properties are applied, usually in order of increasing strength, so that elements are leached according to different mechanisms, e.g. acidification or complexation. This results in a process that is more time consuming than single extractions, but one that provides the partitioning of the total element contents into fractions of different availability [1-4].

Extraction assays allow us to obtain reliable and useful information only if the experiments are correctly planned and executed and if the results are properly interpreted. Extraction treatments give rise to large amounts of data, especially when coupled to rapid multielement analytical techniques, and many research studies also report the main properties of the considered matrices (such as pH, content of organic matter, soil texture) which are important in order to understand their behaviour. The combination of the complexity of the matrices and phenomena under study with the generation

of large data sets renders interpretation difficult. Chemometric techniques can be a valuable tool in connection with single and sequential extraction procedures for several purposes: the development and optimization of the extraction conditions; the calculation of element fractionation; the visual illustration of the experimental results; the acquisition of different areas of information, including relationships among variables, similarities and differences among samples, causes of the observed behaviour (e.g. source identification), models, risk assessment and predictions of future events [5-7]. Chemometrics is deemed to be particularly advantageous when dealing with complex systems, such as soils and sediments, due to the possibility of using multivariate techniques, which take into account the behaviour of multiple variables simultaneously; nevertheless, it should be emphasized that also univariate and bivariate chemometric methods are important, since they remain indispensable for a correct and complete data processing and interpretation, even when sophisticated multivariate techniques are subsequent applied.

This review describes the application of chemometric techniques in research studies involving single and sequential extraction treatments on soils or sediments. Following an overview on extraction procedures, in which both advantages and disadvantages are ascertained, the applications of univariate and bivariate chemometric methods are reported; then the principles of the multivariate chemometric techniques most frequently adopted, the aims of the research studies in which they were used and the main findings obtained with their application will be addressed. In particular, Part I of the review will be focused on variable reduction methods for pattern recognition, one of which, namely Principal Component analysis (PCA), is the multivariate technique most extensively used in conjunction with extraction assays.

To our knowledge, two reviews on element extraction from soils and sediments to date have included a chapter devoted to the application of chemometrics to the experimental results [1-2], but no extensive treatment of this subject currently exists. We are confident that the present work will be of use to researchers interested in adopting the powerful tools of chemometrics in order to exploit the potentialities of single and sequential extractions of elements from solid matrices.

2. Overview on single and sequential extraction procedures

2.1. Single extractions

The main extracting reagents used in single extraction procedures can be classified, according to their chemical properties, as:

- ligands, mainly diethylene triamine pentaacetic acid (DTPA) and ethylene diamine tetraacetic acid (EDTA); despite concerns of being over-aggressive for this purpose (see next paragraph), they are employed for the purpose of estimating plant-available fraction of elements [9-11]. The Standards, Measurements and Testing (SMT) Program (formerly BCR) developed and validated a single extraction protocol (0.05 M ammonium EDTA, one hour, room temperature) [12];
- unbuffered salts, called ‘soft’ or ‘mild’ extractants, such as $\text{CH}_3\text{COONH}_4$, CaCl_2 , NaNO_3 and BaCl_2 . A SMT protocol exists (0.01 M CaCl_2 , three hours) [4]. They are regarded as more suitable than more aggressive extractants, such as chelating agents and acids, to predict the plant-available fraction of elements: therefore the use of unbuffered salts has notably increased over the last ten years [13-16];
- diluted mineral acids, e.g. 0.05 M HCl, or low molecular weight organic acids, such as malic and citric acids; the latter are secreted as metabolic products through plant roots, hence they are believed to simulate natural conditions [17-19]. Some researchers measured element mobilization by the Toxicity Characteristic Leaching Procedure (TCLP), the US EPA’s method for testing waste toxicity [20], which involves a single extraction with diluted acetic acid and sodium hydroxide [21]. Acids at high concentrations (e.g. 6 M HCl) were also used to evaluate the mobile portion of elements [22], but this procedure is not so common.

2.2. Sequential extractions

The most popular sequential extraction procedures are Tessier’s and BCR schemes, which are summarized and briefly commented in Table 1 together with the other procedures adopted in the papers cited in sections 4 and 5. Tessier’s protocol provides the partitioning of elements into five

operationally defined fractions: exchangeable; bound to carbonates and specifically adsorbed; bound to oxides of iron and manganese; bound to organics and sulphides; residual [23]. As with the other sequential extraction schemes, a decrease of element availability during extraction sequence is presumed. Whereas the first fraction is quite labile and therefore easily available for plant uptake, the fifth consists of elements with low mobility and which are unlikely to be solubilised under natural conditions over a reasonable period of time. It should be pointed out that in many of the procedures reported in Table 1 the so-called “residual” fraction is actually a “pseudo-residual” fraction; this happens when it is determined by means of strong acid extraction (e.g. aqua regia) and not after total mineralization as in Tessier’s scheme, which involves the use of HClO_4 and HF .

The BCR protocol was developed by the SMT Program within the framework of a collaborative project, with the purpose of harmonizing the quantification of the extractable trace-metal contents in soils and sediments [3]. The first version of the showed a low reproducibility in interlaboratory exercises, so it was revised by changing the concentrations of some reagents and some operative conditions. Three fractions are obtained with the BCR scheme: exchangeable, water and acid-soluble; reducible; oxidisable; in the revised version, a fourth step of digestion with aqua regia is recommended, even if it is not officially part of the protocol, in order to permit calculation of the recovery by comparison between the sum of the amounts extracted into the four fractions and the pseudo total content obtained by aqua regia digestion [1,17,24-26]. The BCR scheme has shown steady increase over time due to its advantages over other current sequential protocols. Notably, the scheme takes less time and is simpler than Tessier’s procedure, and enables comparability among data obtained in different laboratories with different samples. This is thanks to a method that includes a detailed and highly methodical procedure for the preparation of the reagents and implementation of the extraction process, therefore enabling a uniform approach in different laboratories, and the availability of a standard reference material for the validation of the results.

Many other sequential extraction procedures were developed; most of them bear close resemblance to BCR and Tessier’s protocols and, indeed, have been fashioned on these procedures. Notably, an

additional first stage can be added to Tessier's scheme so that it would be possible to measure the water-soluble element fraction [27]. A number of procedures differ mainly in the reagent used to evaluate the exchangeable fraction (e.g. 1 M KNO_3 , 1 M $\text{Mg}(\text{NO}_3)_2$, 0.01 M NaNO_3) or to extract elements bound to organic matter (e.g. 0.1 M $\text{K}_4\text{P}_2\text{O}_7$ or a mixture of KClO_3 , 12 M HCl and 4 M HNO_3) [27-31]. Finally, other methods attempt to distinguish between elements bound to Mn and to Fe oxides, using different concentrations of reducing agents or different temperatures [28-30, 32].

The BCR protocol was used in many of the studies on sequential extractions cited in this review, as a confirmation of its popularity [33-44]. Other studies were based on different schemes, which in many cases reproduce Tessier's protocol but differ in the first steps [40,44-54]. Some procedures were designed for the fractionation of single elements, such as Hg [55] or P [53,56-59].

Other forms of sequential extraction yield the so-called bioaccessibility, that is the fraction of a chemical that is liberated in relevant biological fluids, such as gastrointestinal content or perspiration, and would be available for absorption [60-63]. They usually involve two steps, simulating the conditions of digestion in the stomach and in the small intestine respectively. Some examples of chemometric treatment of bioaccessibility data will be cited in Part II of the review [64-69]. A different approach to sequential extractions is the use of non-specific reagents coupled to chemometric data treatment, which will be described in Part II [66,69-74].

Most extraction procedures are designed for cations and are not completely suitable for As, owing to its presence in anionic form in soils and sediments. Some sequential extraction methods for As exist, which are based on its similarity with P [75,76].

It is important to note that sequential extraction procedures have several drawbacks, in particular the nonselectivity of reagents and the occurrence of readsorption and redistribution phenomena along the extraction sequence [77]. In addition, the procedures (especially in the batch mode) are time-consuming, and the results are influenced by the experimental conditions adopted (method of sample drying, shaking device...). As the extracted fractions are operationally defined, their association with matrix components is often questionable [1,4]. However, putting aside the

schemes' limitations, it must also be said that valuable information on the behaviour and mobility of elements can be achieved, and such procedures aid in establishing potential risks to the environment, food chain and consequently human health.

A IUPAC report, mentioned by Bacon and Davidson in their review “Is there a future for sequential chemical extraction?” [1] affirms: “despite some drawbacks, sequential extraction methods can provide a valuable tool to distinguish among trace element fractions of different solubility related to mineralogical phases” [78]. We fully support Bacon and Davidson’s conclusions that sequential extractions will have a healthy future in the 21st century, but that their results will be useful only if they are interpreted with full awareness of their limitations [79].

3. General considerations

3.1. Terminology

We will use the term “elements”, instead of more specific words, such as “metals”, “trace elements”, or “potentially toxic elements”, in order to cover all the types of analytes considered in the studies described, including nonmetals such as As and Se, or major metals such as Fe, Ca and Mg.

We will follow recommendations by the IUPAC and refer to the results of single and sequential extractions as “distribution” or “fractionation” of elements, avoiding the term “speciation”, which was common until about ten years ago, but is nowadays referred to the determination of well-defined chemical species, e.g. organometallics or metals with different oxidation states [3]. We will not give any judgement on the suitability of the extracting solutions used, or on the correspondence between the definition of the extracted fractions and the actual content of the extracts, as our focus is the data treatment techniques.

We will refer to “main properties” to indicate one or more physico-chemical characteristics of soils or sediments, like cation exchange capacity (CEC), pH, organic matter, texture, total nitrogen, electrical conductivity, etc., when some of them are investigated in the cited papers.

In most chemometric techniques the data are arranged in matrices: each row corresponds to an "object", i.e. a sample, and reports the values of the "variables", or "features", i.e. the concentrations of the analytes, in that sample.

3.2. Analytical aspects

The methods of determination of the elements present in the extracts are well established. Table 2 shows that most authors used atomic spectroscopic techniques, mainly ICP-AES, which has the advantage of being more rapid than FAAS and GFAAS, despite having a lower sensitivity than the latter. Furthermore, ICP-MS was used in some researches; the high concentrations of dissolved solids present in many extracts may be a drawback with this technique, but its high sensitivity allows the dilution of the sample solutions before analysis.

Quality control of the experimental results for sequential extraction is assessed by comparison between the total content and the sum of the extracted fractions [51,80] or, for the BCR scheme, by using a standard reference material certified for the extractable content, BCR CRM 701, lake sediment [36,38,41].

Most of the studies cited in this work used the conventional batch procedure for the extractions, but some examples of column leaching are also reported [81-83]. In fact, the use of flow-through dynamic approaches has been increasing over the last decade [84-86]. This is because they provide a better simulation of natural conditions and give information on the kinetics of element mobilization; in addition, they are seemingly less affected by the drawbacks of batch extraction procedures, in particular by analyte readsorption, and enable the on-line coupling of the extraction and determination stages. Of course, the chemometric techniques described in this work are suitable for application to the results of dynamic procedures.

3.3. Chemometric aspects

We covered the literature from 2000 to 2009, searching through ISI Web of Knowledge with combinations of the following keywords: extract*, fraction*, mobil*, leach*, speciat*,

chemometri*, multivar*, soil*, sedim*. Table 2 summarizes the main features of the papers considered in sections 4.1, 4.2 and 5 of the review: the type and location of the investigated samples; the elements determined; the extraction media; the analytical method used for the determination of the extracted elements; the chemometric technique(s) applied; the software package used. In this review (Part I and Part II) the various chemometric techniques will be discussed one by one, hence the studies using two or more of such techniques will be mentioned two or more times.

Presently, whereas chemometric techniques are extensively used to process data on total element concentrations [e.g. 8,38,87-90], they are less commonly applied to single and sequential extraction results. Different approaches can be distinguished: i) in most cases, chemometrics is used as a tool for the interpretation of the experimental results, in order to describe the properties of the investigated system or for risk assessment; ii) some papers take a counter approach, being focused on the testing of a chemometric technique, and use a data set mainly as a means to demonstrate the efficiency of such technique [8,42,43,91]; iii) other studies use chemometrics in order to calculate the partitioning of elements among different components of soils or sediments [66,69-74]; iv) in a few cases, experimental design was used in conjunction with sequential extractions to optimize the experimental conditions or to study their effect on extraction efficiency [70,71,92,93].

The principles and applications of the chemometric techniques considered in this review will be described in the following sections, and only few hints on their mathematical aspects will be given. It should be stressed that most of such techniques can be applied only if the data fulfil some requirements, e.g. normal distribution: such requirements can be found in textbooks and handbooks on chemometrics.

Only the findings obtained with chemometrics on extraction assays will be reported, while other results, for instance about total concentrations, will be omitted. We will also omit the numerical details on the results reported by the authors, such as the percentage of variance explained by principal components (see section 5.1.1): nevertheless, we underline that such details are important,

within a study, for a correct interpretation of the results and assessment of their validity.

Most of the studies cited in this paper use chemometrics for data visualization and interpretation, so we will treat this topic in Part I of the review, then (Part II) we will describe the applications of chemometrics to the characterization and optimization of the extractions and to the calculation of element partitioning.

4. Univariate and bivariate techniques

Chemometrics comprises not only multivariate techniques, but also bivariate and univariate statistical methods, which find wide and crucial applications to the processing of results for extraction assays. First of all, the calculation of concentration means and standard deviations is obviously a prerequisite of any discussion and interpretation of data. Furthermore, sequential extraction procedures must sometimes be checked regarding one analyte because it is of particular importance, for instance for its toxicity. Preliminary statistical tests are sometimes carried out before applying multivariate data processing, e.g. using the Kolgomorov-Smirnov test in order to check for normal distribution [37,53,55,57,58,94-110]. A number of papers report the preprocessing of the data, such as the replacement of missing values, the identification and elimination of outliers, the transformation of data [35,36,40-42,49-51,56-59,66,70,71,81,83,91,94,95,99-101,106,107,109,111]. For instance, log10 transformation is usually carried out in case of deviation from normal distribution; data are often scaled by column-standardization, i.e. subtracting the column means from each value and dividing by the standard deviation [5].

ANalysis Of VAriance (ANOVA) and correlation analysis are treated in more detail hereafter owing to their valuable contribution to the interpretation of experimental results. The examples reported are taken from the papers cited in section 5, i.e. are referred to studies in which these techniques were used in conjunction with multivariate techniques.

4.1. ANOVA

ANOVA tests for the presence of systematic differences between groups of data differing for the value (“level”) of one or more parameter (“factor”). Factors can be experimental conditions (temperature of sample treatment, pH, laboratory...) or other situations (sampling time, presence of traffic, contamination...) [5-7]. The total variance of the data (calculated as the sum of squares of the deviation of the data from the total mean, named “grand mean”) is split into two contributions, i.e. within-groups and between-groups variance. Such contributions are compared with an F-test: if a significant difference is found, then it can be concluded that the factor has a significant effect on the data. If a single factor is being investigated, one-way ANOVA is performed. In the presence of two or more factors, two-way or multi-way ANOVA are used.

ANOVA is a very important tool to describe differences between different extraction steps, or between samples or elements; it can be used to examine environmental properties giving rise to differences in a dataset, such as the presence of spatial or temporal variations. When data do not follow normal distribution, non-parametric ANOVA can be used. The following examples show some possible applications of ANOVA. Katsaounos et al. [58] used non-parametric ANOVA (Kruskal-Wallis ANOVA) in order to study the seasonal trend for P in fractions extracted from river sediments by testing for significant differences in sampling dates. The results of ANOVA were combined with those of the median test. The combination of these methods was shown to provide a more representative description of seasonal patterns in complex data sets than discriminant analysis (see Part II). A similar application of non-parametric ANOVA was reported by Kaiserli et al. [56], who demonstrated that the sampling month had a significant effect on P fractions in lake sediments. A different approach to data treatment was used by Alvarenga et al. [37], who applied parametric or non-parametric ANOVA depending on the results of Kolmogorov-Smirnov test for homogeneity of variance and normality. They studied the effect of organic amendments on a contaminated soil: when ANOVA revealed the presence of significant differences between samples, they applied a post hoc Tukey honest significant difference test to further elucidate such differences.

An example of extensive use of ANOVA is the paper by Bleeker et al. [112], who referred to the results of this technique, in terms of significant differences between sites, throughout their study on the effect of variations in metal availability on earthworms. They did not give indications on how ANOVA was carried on.

Yun et al. [111] used 2-way ANOVA to study the spatial (sampling site) and temporal (sampling month) variations in element concentrations in roadside sediments. A remarkable aspect of their study is the coupling of ANOVA with factor analysis (see section 5.2.2): the latter permitted to identify the phenomena causing the variations identified with the former, such as leaching by rain and vehicular traffic.

4.2. Correlation analysis

Correlation analysis is a bivariate technique for the measurement of the degree of association between two variables [5]. The strength of the association is usually expressed with Pearson's correlation coefficient (r):

$$r(x_1, x_2) = \frac{\text{cov}(x_1, x_2)}{s_{x1}s_{x2}} \quad (1)$$

where

$$\text{cov}(x_1, x_2) = \frac{\sum (x_1 - \bar{x}_1)(x_2 - \bar{x}_2)}{n - 1} \quad (\text{covariance}), n = \text{number of data}$$

and

$$s_x = \frac{\sum (x_i - \bar{x})^2}{n - 1} \quad (\text{standard deviation})$$

In the presence of data not normally distributed, the non-parametric Spearman rank correlation coefficient can be used:

$$r = 1 - \frac{6 \sum d_i^2}{n(n^2 - 1)} \quad (2)$$

where n = number of paired observations and d_i = difference between the ranks given separately to the two variables.

Obviously, a correlation between two variables does not automatically imply a relationship of cause and effect between them, and the meaning of such correlation must be interpreted taking into account the knowledge on the investigated system.

As table 2 shows, most of the papers considered in this review report the use of correlation analysis, which remains the workhorse of many studies. The correlation between variables was used in order to study the relationship between: i) two different elements extracted with a single reagent [22,102,107,111,113,114], or the contents of a single element extracted with two different single reagents [115] or with two different procedures [39]; ii) two different elements released in the same fraction in a sequential extraction procedure [48,116], or the amounts of the same element released in different fractions [47,52,95]; iii) available and total amounts [44,104,110,111,117-120]; iv) extracted elements and main soil properties [35,50,51,55,57,82,83,91,95,98,102,104,105,108,110,113,114,117-124]; v) element contents in plants and in soil extracts [33,37,57,100,125,126]; vi) element contents in different soil horizons [127].

The values of correlation coefficients are useful in order to make hypotheses on the sources or on the chemical and environmental behaviour of elements.

An example of proper interpretation of correlations is the paper by Pérez et al. [35], who commented the associations between element fractions and major soil components in terms of sources or chemical behaviour: for instance the correlation of residual Pb with Fe_2O_3 suggested its inclusion within resistant crystalline structures. Lucho Constantino et al. [51] reported another interesting example of result interpretation: they explained the relationships among soil main properties and element contents in fractions taking into account phenomena occurring in soils, such as adsorption and ion exchange. On the other hand, correlations among elements in a fraction were interpreted by Yu et al. [48] as indications of a common source.

Finally, it should be recalled that the calculation of correlations is part of the mathematical

treatment of many multivariate techniques, such as those reported in section 5.

5. Visualization and interpretation of experimental results

The topics of visualization and interpretation of experimental results will be treated together, because in many cases the same chemometric technique is used for both purposes.

5.1. Principal component analysis

PCA is the multivariate technique most extensively used for processing the results of single and sequential extractions (see Table 2). This happens because it is relatively easy to apply, using the commercial software packages, the interpretation of the data is relatively simple and provide useful information.

5.1.1. Principles

PCA is an unsupervised pattern recognition technique, i.e. a technique for classifying objects into classes that are not established *a priori*. It is based on variable reduction through the calculation of the so-called Principal Components (also named "factors" or "latent variables"), which are linear combinations of the original variables [5-7]. Therefore, in the presence of m variables (V_1, V_2, \dots, V_m) the i^{th} principal component will be

$$PC_i = w_{i1}V_1 + w_{i2}V_2 + \dots + w_{im}V_m \quad (3)$$

where $w_{i1} \dots w_{im}$ are the loadings, i.e. the weights of the original variables on the linear combination. PCs are not correlated with each other and altogether explain the total variance of the data. The percentage of explained variance decreases from the first PC to the second and so on. In PCA, the original data matrix X ($n \times m$), where n rows correspond to n samples and m columns correspond to m variables) is decomposed as a product of two matrices:

$$X = R W^T \quad (4)$$

where R ($n \times m$) is the matrix of the scores, i.e. the coordinates of the samples on the PCs, and W^T ($m \times m$) is the transpose of the loadings matrix.

Since the first principal components retain most of the variance, many variables can be summarized by a few components [128] and a plot of the first two or three PCs enables one to visualise most of the information contained in the data. Therefore, PCA can also be considered as a technique of projection of a data set to a lower dimensional space. The choice of the number of significant PC can be made with various criteria. If h PCs are retained, the loss of information can be expressed by introducing a matrix of residuals E :

$$X(n \times m) = R(n \times m) W(m \times h)^T + E(n \times m) \quad (5)$$

A rotation of PCs can be carried out, usually with the Varimax method, yielding an increase of the weights of higher loadings and a decrease of the weights of the lower ones, thus allowing an easier interpretation of the results.

5.1.2. Applications

The main findings obtainable from the examination of the values of scores and loadings, or of the corresponding plots, are:

- the visualization of multivariate data in two- or three-dimension plots;
- a classification of the objects. The samples with similar scores are close in the score plot: they have similar composition, reflecting similar characteristics, and vice versa. The anomalous samples are far from the other ones, and they could indicate the presence of a polluted “hot-spot”, or conversely of a cleaner area within a contaminated site, or even an analytical error;
- the positive or negative correlations among variables, which suggest their mutual influence or the presence of some common, or opposite, characteristics, such as chemical properties or source (anthropogenic or natural); when PCA is coupled to correlation analysis, it permits to visualize and confirm the computed correlations between variables;
- the relationships between objects and variables, observable from the combined plot of scores and loadings, which enable to identify at a glance the samples with high or low concentrations of some elements; however, the use of biplots is discouraged by Einax et al. [6];

- the grouping of variables into factors, which represent phenomena influencing the composition of the samples, e.g. anthropogenic activities or natural processes; factors can be interpreted depending on the characteristics of the variables;
- the influence of each variable on the PCs: variables with high loadings have a high influence on the PC and vice versa.

Examples of applications of PCA are given hereafter.

The aim of several studies on soils or sediments is the identification of the sources of elements, in particular the differentiation between natural and anthropogenic ones. An example of the use of PCA for this goal is the paper by Filgueiras et al. [34], who applied the BCR sequential extraction scheme to river sediments. An interesting aspect of their study is that both the concentrations of extracted elements and of the sediment phase related to each fraction (e.g. CaCO_3 , Fe_2O_3 , MnO) were considered. The authors discussed the variable loadings on the factors, assuming that the binding behaviour of the elements indicates the occurrence of different pollution sources and hypothesized the following sources: discharges of human origin for Pb and Cu, which were associated to organic matter, and traffic emissions for Pb; industrial effluents (e.g. chromium-plating) for Ni and Cr, which were not associated to a particular matrix component, suggesting that they were independent of the sediment composition; diffuse sources for Cd, which had a different behaviour from the other elements and was associated to the Fe-Mn oxide content. The presence of outstanding sampling points in the score plots was explained with the vicinity of some pollution source, such as sewage discharge.

Yu et al. studied element sources in river sediments considering element concentrations alone [48] or in conjunction with sediment phases [46,47]. They just remarked the presence of common sources, but did not identify such sources, probably because the main aim of their paper was different (see below).

Investigation of element sources was also performed by Abollino et al. [38], Riba et al. [49], Bäckström et al. [50] and Relić et al. [52].

PCA represents a useful tool also to investigate the characteristics and behaviour of elements in an environmental compartment. An example of this application of PCA is the paper by Katsaounos et al. [58], who studied the fractionation of P in river sediments and its speciation within each fraction. The discussion of the variable loadings on PCs is a good example of interpretation of the results of PCA in terms of chemical and physical processes, and it permitted to gain insight into the interactions among the fractions and chemical forms of P. Another noteworthy feature of this paper is a detailed description of the procedure used for performing PCA, including the removal of redundant variables, a step which is not usually carried out and can be helpful for data interpretation. Finally, PCA provided a classification of the samples according to their contamination level, which formed the basis for the application of another multivariate technique (linear discriminant analysis) as we will describe in Part II.

The paper by Kaiserli et al. [56] reports another quite interesting discussion of chemometric results in terms of chemical and physical processes. The authors investigated, through the values of the variable loadings, the influence of the most important P-binding elements (Al, Ca, Fe, Mg and Mn) and of other sediment features on the fractionation of P in lake sediments. Probably an examination of scores, in addition to variable loadings, might have given some additional information on the differences between the two lakes.

The discussion of the results made by Yu et al. [46,47] is somewhat simpler than those reported in the previous two papers, but it is anyway of interest for the interpretation of the role of phases in the binding of Co, Cr, Cu, Ni, Pb and Zn: the lack of correlation between elements nominally extracted from carbonates and Mn oxides and the corresponding phases suggested that the latter were not good scavengers in the investigated rivers, whereas organic matter and Fe oxides were more accessible to elements; these results were interpreted as a competition among various sediment phases for binding with elements.

Other applications of PCA to studies on the behaviour of elements in environmental compartments are reported by El-Nemr et al. [22] for muddy and sandy marine sediments, by Relić et al. [52] for

rivers sediments and by Praveena et al. [129], who distinguished between mangrove lagoon sediments at high and low tide.

PCA can be used to differentiate samples according to their composition. Our research group [38] studied element distribution in a marine sediment core. First of all, we selected the layers of the core to be treated with the BCR scheme with the aid of the results of PCA and HCA for total concentrations, so as to examine one specimen for each of the sample groups evidenced with such techniques. PCA was then applied to the fractionation results. The score values showed a differentiation between the surface and bottom samples for the first three fractions, but not for the fourth one. This suggests that the minerogenic component of the core, mainly associated to such fraction, was similar in all sections, while the more available fractions had a larger variability over the length of the core, i.e. over time. The top layer of the core was distinctly differentiated from all the others, probably because it is directly in contact with the water column. The results of PCA, combined with those obtained for total concentrations, suggested a separation between higher and lower sections of the core associated to a stronger fingerprint from biogenic and geological processes, respectively.

In another study [88] we examined the fractionation of elements in agricultural soil profiles from five different areas. The results of PCA showed that samples were mainly grouped according to the sampling site, indicating that the soil properties influenced the behaviour of elements towards extraction. The top horizons of two sites markedly differed from the lower ones, possibly because of the effect of agricultural treatments. These observations might have been made also by examining the values of the data, but the results of PCA allowed us to visualize these features more easily and more rapidly. Positive and negative correlations among variables were also discussed. Pérez et al. [35] adopted a different approach to identify groups of samples with different element mobility and availability within a contaminated soil, since they took into accounts scores, loadings and the results of HCA (see part II). A remarkable aspect of their paper is the clear explanation of the criteria used in the classification.

The results of PCA can contribute to the characterization of contaminated sites, as shown also by the paper just cited [35], and to the evaluation of the effectiveness of decontamination treatments. Riba et al. [49] analyzed estuary and river surface sediments and a sediment profile from an area affected by the well-known and extensively studied mining spill in Aznancóllar, Spain. The associations of the variables with the factors were extensively discussed and profitably used to hypothesize the origin and evolution of contamination, notably to distinguish between the effect of the mining accident and of chronic pollution. Interestingly, some pollution indexes (ecological risk factor and surface enrichment factor) were inserted as variables, in addition to element concentrations and main properties.

Lucho-Constantino et al. [51] studied agricultural soils irrigated with raw wastewater. A remarkable feature of their paper is the interpretation of the meaning of the factors. For example, PC1 was associated with electrolytic conductivity, alkali and alkaline earth elements, anions, a few trace elements and total nitrogen: it was supposed to represent a "salinity variable".

Our research group used PCA to characterize an industrially polluted soil [80]. Fig. 1 shows the combined plot of scores and loadings for the third fraction of Tessier's scheme (the original sample coding was maintained). We will comment this figure in detail in order to show how it can be interpreted, using samples scores to differentiate sampling points and variables loadings to gain insight into element behaviour or sources. Surface (A1-A14) and vertical profile (A17b-A31) samples are in opposite areas of the plot, with one exception (A19). The latter are characterized by higher percentages of the elements of mainly geochemical origin (Sc, Ti, La, Y and Al) and lower levels of the elements known (from a previous study [89]) to be main pollutants of the investigated soil, i.e. Cd, Pb and Zn; they can be further split into two sub groups (A17b, A20, A21b, A 24 and A28; A23, A26, A27, A29, A30 and A31); the separation is fairly related to collection depth, indicating the heterogeneity of the soil material. Sample A25, corresponding to the 190-218 cm soil layer, is distinctly separated from all the other samples because of the high percentages of extracted La, Sc, Ti and Y. Regarding variables, the loadings of Cd, Pb and Zn on PC1 have opposite sign

with respect to the other variables, suggesting a competition between the main pollutants and the other elements for binding to Fe and Mn oxides. The correlations between Sc and Ti and between Y and La may be due to a common geochemical origin, whereas the lack of correlation between Fe and Mn suggests the presence of two different mechanisms of dissolution of their oxides.

In a previous work we treated a profile of the same soil and one profile from another industrially-polluted soil by single extractions [89]. In both cases, the sample scores showed differences among samples associated to depth of collection. When data from both sites were treated together, a clear separation between the extracts from the two soils was apparent.

Fig. 1. Combined plot of scores and loadings obtained by PCA for pH and element percentages extracted from contaminated soil samples (coded A1-A31) into the third fraction of Tessier's procedure, after column standardization [80].

Alvarenga et al. [37] studied the effect of the addition of three organic residues on element availability and main properties of a contaminated soil. They made a clear interpretation of the combined plot of scores and loadings, which allowed them to well distinguish among soils treated with different amendments and to visualize the effects of the latter. For instance they observed a decrease in the mobile fraction of Cu, Pb and Zn and an increase in pH and organic matter upon amendment addition.

The application of PCA to investigate the relationships between soil and biota is less common, since this subject is often studied with other chemometric techniques, such as multiple linear regression (see part II). Variable loadings rather than scores are usually considered in these kinds of studies. Tokalioğlu and Kartal [33] used PCA to compare the element content in vegetables and in the BCR first fraction (acid-soluble elements) extracted from urban garden soils where the vegetables were grown. The results were not completely satisfactory, as they did not observe clear associations between plant and soil contents; in our opinion, the paper is however of interest as an example of interpretation of the meaning of PCs, which revealed the influence of urban traffic

(PC1) and agricultural treatments (PC2). On the other hand, in a subsequent work of the same research group Tokalioğlu et al. [125] found significant relationships between element concentrations in grape plants and in soil single extracts using correlation analysis, PCA and HCA: it was concluded that the extractable portions of metal was readily available to plants.

A similar use of PCA was made by Maiz et al. [94]: the examination of variable loadings on factors showed the presence of relationships associations between element contents in grass and in soil fractions obtained with a short sequential extraction procedure developed by the authors. They thus concluded that the short procedure is suitable for studying availability in polluted soil-plant systems.

Finally, Bleeker et al. [112] assessed element bioavailability with test organisms, namely earthworms, and used PCA to evaluate the association among the soil main properties, the total and extractable element content and the biomass of earthworms.

A further field of application of PCA is the evaluation or optimization of a procedure for sample treatment or data processing.

Bäckström et al. [50] applied PCA to compare dry weight- and LOI (loss on ignition)-normalized sequential extraction results for roadside soil samples: the variable loadings for the LOI-normalized data were found to better discriminate anthropogenic and lithogenic elements than those from dry weight-normalized data. In addition to the usual combined plot of PC1 vs. PC2, the authors represented the data with an original approach, plotting variable loadings on PC2 vs. the cumulative leachable fraction percentage; as Fig. 2 shows, the elements are almost completely lined up (r^2 0.76), with anthropogenic elements (e.g. Pb, Cu and Zn) having high loadings and lithogenic ones (e.g. Al, K and Mg) having lower ones. Another interesting aspect of the paper is the validation of results with the leave-one-out procedure [5].

Fig. 2. Loadings from PC2 based on LOI-normalized data (all fractions) for roadside soil samples versus the leachable fraction (averages for all 16 samples calculated on a dry weight basis) for all elements. Correlation coefficient, $r^2 = 0.76$. (From [50] by permission of Springer).

Wang et al. [116] compared the score plots obtained for river sediments considering total and extractable concentrations respectively, and observed that the distinction between polluted and unpolluted samples was different for some samples in the two cases. This finding confirms the importance of determining element mobility in addition to total concentrations.

Madrid et al. [36] used PCA and linear regression in order to assess the associations between the amounts of elements extracted by single extractions and the BCR protocol (sum of the first three steps) from urban soils. The equivalence between the two methods was judged to be incomplete, so the authors concluded that dilute HCl was unlikely to be a suitable alternative to BCR procedure to estimate potential mobility and extractability of elements.

Obviously PCA, as well as the other chemometric techniques considered in this review, can be applied not only to soils and sediments, but also to other matrices, such as sewage sludge, atmospheric particulate matter and fly ash. A few examples are given here.

Pérez Cid et al. [39] used PCA (together with other mathematical methods) to compare the performances of two extraction procedures for an urban sewage sludge and a sludge from an olive oil factory; Handt et al. [45] utilized the trends of the variable loadings to support their hypotheses on different sources of elements (industry and traffic) in dust samples; Pardo et al. [130] studied the mobility of elements precipitated as ferrite from polluted effluents, showing a distinction between magnetic (crystalline) and non-magnetic (amorphous) samples from PCA scores and a differentiation of Cr from all the other elements from loading values.

Even if most applications of multivariate techniques to extraction assays were published since 2000, some papers on this subject appeared before that date, mainly regarding PCA. An example is the paper by Pardo et al. [131], who discussed the values of loadings and scores for the residual fraction of Tessier's scheme in river sediments, assuming that such fraction is smaller in polluted than in

unpolluted rivers. They processed their own experimental results together with literature data on river sediments: this approach is not so common and it could be fruitfully applied also in recent studies.

In general, three main ways of processing data on sequential extractions were adopted in the above-cited papers: i) the amounts (or percentages) extracted into each fraction were processed separately [33,34,35,38,46,47,48,52,80,88,130,131]; ii) the data on all fractions were treated simultaneously [36,45,49,50,51,56,58,116]; iii) the sum of the first fractions [39,52,94,116]. In our opinion the most proper procedure depends on the aim of the investigation. If the chemical behaviour of elements or the individuation of sources is of interest, then the separate treatment of the data from each fraction is advisable. The inclusion of all fractions in the same PCA is necessary when differences among fractions are to be pointed out; for instance Wang et al. [116] found that the residual fraction was distinctly different from the other ones, suggesting the different mobility of elements bound to it. This mode of data processing can be adopted also when the focus is sample differentiation from score values. Finally, the cumulative amounts extracted in the first fractions, which is supposed to represent the available proportion of elements, are reported when risk of pollutant release is evaluated.

Furthermore, the dataset can contain only element concentrations [22,33,38,39,45,48,50,52,58,94,116,125,130], or include main sediment or soil properties [34,35,36,37,46,47,49,51,56,80,88,89,129,112,131]. Whereas it is always advisable to take main properties into account, for a better characterization of the matrix under study, this is not indispensable in some applications, for instance when the contamination level is estimated, a decontamination technique is tested or a procedure for sample treatment or analysis is evaluated.

5.2. Factor analysis

5.2.1. Principles

The goal of factor analysis (FA) is to find common factors explaining the experimental results [5-7,

132]. The total variance of the data is divided into three parts: common feature variance, specific feature variance and residuals or errors. Factors represent the common variance of features. In FA the data matrix X is decomposed as:

$$X = FL^T + E \quad (6)$$

where F is the score matrix, L^T is the transpose of the loading matrix L and E expresses specific feature variance and residuals.

Common variance is expressed by the value of the communality, i.e. the part of the variance of one feature which is described by the common factor solution in the factor analysis. Various criteria can be used to choose the number of significant factors and disregards the last ones, which are supposed to express noise. After factor rotation, the nature of the variables most heavily contributing to each factor enables to identify its meaning. Examples of factors influencing element extractability in soils are agricultural practices, atmospheric fallout...

5.2.2. Applications

FA has been less extensively applied than PCA to single and sequential extraction results. The aims of the studies using this technique are analogous those described by PCA, i.e. identification of sources, characterization of chemical behaviour of available elements, evaluation of an experimental procedure.

Arcega-Cabrera et al. [54] used FA to gain insight into the geochemical processes involving Pb in river sediments. Two remarkable aspects of their paper were i) the discussion of variable contributions to factors, based on the relationships between the bioavailable element portion and the main sediment properties; ii) the separate calculation of FA for dry, rainy and post-rainy seasons, in order to study the temporal variations of Pb geochemistry.

The paper by Yun et al. [111] on contaminated roadside sediments is an example of application of FA to the identification of sources and of causes of spatial and temporal distribution of elements. It is interesting to note that the authors included some non-chemical variables in the data-set, notably

traffic density, percentage of metal industries and monthly precipitation, which actually may have a great influence on sediment composition. The interpretation of variable loadings on factors was in agreement with the results of ANOVA (see section 4.1).

Cukrowska et al. [81] adopted a column leaching approach for the investigation of tailings damp materials from gold mines and demonstrated the suitability of such procedure by FA. The meanings of the factors were related to properties of the damp material, such as its solubility and the redox conditions. The score plots showed the differences among the layers of the damp, among leachates collected in two subsequent days or obtained with extractants at different pH.

Other examples of application of FA are the papers by Dalurzo et al. [53], who studied the characteristics of Alfisols, Ultisols and Oxisols soils, and by Illmer et al. [97], who identified three biotic and three abiotic factors in forest soils; such factors were interpreted by multiple linear regression (MLR) as described in Part II.

5.3. *N-way methods*

5.3.1. *Principles*

Sequential extraction results are multidimensional, i.e. are defined by samples, elements and fractions and can be arranged in a three-way data array consisting of rows, columns and layers. In some studies, such data were treated with multi-way data analysis techniques, in order to extract more information than that obtainable with bidimensional methods [40-42,133]. Three approaches were followed [5]:

- the simplest one is named matrix unfolding or matrix augmentation (MA), and is not a real multiway method; the three-way data array X ($i_{\text{samp}} \times j_{\text{el}} \times k_{\text{frac}}$) is unfolded into a two-way array X_{aug} ($(i_{\text{samp}} \times k_{\text{frac}}) \times j_{\text{el}}$), which is then treated with the conventional procedures of PCA, so that each element x_{ij} can be expressed as:

$$x_{ij} = \sum_{f=1}^r u_{if}^{\text{aug}} v_{if} + e_{ij} \quad (7)$$

where u_{if} and v_{if} are the elements of the scores and loading matrices U_{aug} and V , r is the number of components retained and e_{ij} is the error term.

Unfortunately, the information on samples and fractions is confounded with this procedure. A method of re-folding the matrix in order to separate the information has been proposed [134,135].

- Another approach is Parallel Factor Analysis (PARAFAC), which is based on the decomposition of a three-way data array X ($i \times j \times k$) into three loading matrices A ($i \times r$), B ($j \times r$) and C ($k \times r$), so that

$$x_{ijk} = \sum_{f=1}^r a_{if} b_{jf} c_{kf} + e_{ijk} \quad (8)$$

where r is the number of factors retained and e_{ijk} is the residual error term.

The choice of the value of r is critical and can be made with various criteria [40].

- Finally, Tucker3 method is based on the decomposition of the matrix X into a three-way core matrix G and three two-way loading matrices $A(i \times P)$, $B(j \times Q)$, $C(k \times R)$:

$$x_{ijk} = \sum_{p=1}^P \sum_{q=1}^Q \sum_{r=1}^R a_{ip} b_{jq} c_{kr} g_{pqr} + e_{ijk} \quad (9)$$

where P , Q and R are the numbers of factors assigned to each mode (in this case, modes are information about samples, elements and fractions) and g_{pqr} are the elements of matrix G ; g_{pqr}^2 represents the interactions among the three modes. An advantage of Tucker3 method over PARAFAC is that different numbers of factors can be used for the different modes.

N-way methods can be used also with other kinds of multidimensional data, for instance deriving from a single extraction on different layers in a soil profile [133]. The following examples will help clarify the mechanism of multiway analysis.

5.3.2. Applications

Presently there are not many application of N-way methods to extraction results, but the use of this technique will probably increase in the future, owing to its potentialities. Due to its being relatively “new”, it is not surprising that some papers, in addition to studying the characteristics of the

samples of interest, dedicated much attention to the procedure followed for the calculations or compared the performances of more data treatment techniques.

Three interesting aspects emerge from Pardo et al.'s paper [41], in which MA, Tucker3 and PARAFAC were applied to the results of BCR scheme for soil samples. The first one is a comparison among the three chemometric techniques, which showed that the information obtainable increased in the order $MA < PARAFAC < Tucker3$. The good performance of Tucker3 method was due to the possibility of choosing different numbers of factors for each mode ($A =$ samples; $B =$ variables; $C =$ fractions). A second issue is the interpretation of the outcomes of the three techniques, which led to a characterization of the investigated soil in terms of distinction among sampling points, description of element behaviour and of discrimination between predominant and minor fractions. Finally, the authors searched for a single parameter that could model the potential environmental hazard of individual soils; they found that samples could be classified according to their Tucker3 A-mode loadings, and reported a contour map of the loading values in the physical space, showing the most potentially hazardous areas.

In a previous work Pardo et al. [136] applied MA and PARAFAC to sequential extraction results for marine sediments. They could not use Tucker3, because it requires a superdiagonal core matrix G , a condition which was not fulfilled with their dataset. MA provided information on elements and fractions but not on the global behaviour of sampling points, whereas PARAFAC covered all the three aspects. Fig. 3 reports the loading plots for the three modes, showing the relationships among sampling points (A mode), among elements (B mode) and among fractions (C mode). In addition, the authors plotted A-mode loadings of factors 1 and 2 vs. the coordinates of the sampling points, obtaining two contour plots which show areas having different levels of available toxic elements (As, Cd and Ni) and consequently different environmental hazard.

Fig. 3. Loading plots obtained with Multy-way PCA applied to the results of the BCR scheme for marine sediments. (a) A-mode; (b) B-mode; (c) C-mode (From [136] by permission of Elsevier).

Alvarez et al. [40] used PARAFAC to compare the efficiency of three fractionation schemes for the characterization of estuary sediments. Like Pardo et al. [136], they could not use Tucker3 method because the core matrix G was not sufficiently superdiagonal. Again, the three modes provided information on sampling points, elements and fractions.

Stanimirova et al. [42] assessed the performance of Tucker3 method using data on two soil depth profiles collected from a contaminated site. They applied the BCR protocol in two conditions, namely inert and non-inert atmosphere. Tucker3 method was extended to work with a four-way data array (samples from different depths \times elements \times fractions \times conditions). The authors chose the model with complexity [2 4 3 1], i.e. with two factors in the first mode, four factors in the second one and so on. The first mode (A) was related to depth, hence the plot of A1 vs. A2 showed the classification of the samples according to the depth of collection. The second mode (B) was related to the elements and two projections of the four factors (B1 vs. B2 and B3 vs. B4) differentiated them in two groups. The third mode (C) was related to the fractions; the plots of C1 vs. C2 and C1 vs. C3 showed a clear differentiation between the first three fractions and the fourth one. The fourth mode (D) included only one latent factor, and surprisingly did not reveal a difference between measurements in inert and non-inert atmosphere. Then the authors considered the core array: as an example, we will report the meaning of two elements of the core. The most important one explained the interaction among the first factors in all modes: its meaning is that in the top layers the analytes are present in immobile forms; the second most important core element was related to the trend of residual Cd with depth, due to different accumulation pathways: dust precipitation and the flooding of a small stream in the top layers, and direct accumulation in deep ones. The authors concluded that the four-way Tucker model chosen enabled them to obtain some information on bioavailability and behaviour of elements. In our opinion, the paper combines a rigorous data treatment with a proper interpretation of the results in terms of environmental and geochemical processes and is a good example of the potentialities of the application of chemometrics to extractions.

An example of application of N-way analysis to single extraction results is the paper by Singh et al.

[133], who compared the performance of MA-PCA, PARAFAC and Tucker3 in assessing the status of soil profiles irrigated with wastewater. Three-way PCA was more suitable than MA-PCA to interpret the three-dimensional data set ($A = \text{samples} \times B = \text{variables} \times C = \text{depth}$). Similar findings were made with both PARAFAC and Tucker3 on i) differences among sampling sites (highlighting the effect of the distance from the wastewater outlet), ii) elements and main soil properties (identifying wastewater-related elements, i.e. Cr, Cu, Ni and Zn), iii) differences among layers with different contamination levels. Tucker3 method gave further information through the core array. For instance, it was observed that sampling sites receiving highly contaminated wastewater were adversely affected in terms of main soil properties, mostly at depths between 5 and 20 cm. The above examples show the potentialities of N-way analysis for the treatment of multidimensional data, and we presume that its applications will increase in the near future. Both Tucker3 and PARAFAC have advantages and disadvantages. The former is more informative than the latter, thanks to the possibility of choosing the number of factors for each mode and to the presence of the core array, but it is not applicable to all datasets, since the core array must fulfil some requirements. PARAFAC gives a less complete picture of the investigated samples, but its results are easier to interpret than those of Tucker3.

5. Concluding remarks

Chemometrics is a powerful tool for the treatment of single and sequential extraction results. PCA is the multivariate technique most extensively used with these kind of data; its main applications are the investigation of the sources of elements and of their biogeochemical behaviour, the identification of areas with different contamination levels and the assessment of experimental or computational procedures. We presume that the application of N-way methods will increase in the near future, owing to their capability to deal with multidimensional data. It is important to have a good knowledge of the characteristics of the matrix and of the properties of the elements under study, in order to correctly interpret the outcomes of data processing and obtain as much

information as possible from them. The above cited paper reported different data preprocessing or standardizing procedure (or did not mention these steps), different ways to calculate PCA (e.g. with or without Varimax rotation), choosing the number of significant factors and interpreting the results. As the need for harmonization of experimental procedures led to the BCR sequential extraction procedure, so a harmonization of the chemometric data treatment procedures would be desirable, in order to improve comparability among results. In general, the application of more than one technique to experimental results can be useful to confirm or exclude an hypothesis or to examine data from different points of view; examples of studies adopting two or more chemometric methods will be reported in Part II of the review.

The variable reduction techniques described above can be adopted also by researchers who are not expert in chemometrics, using commercial software packages. However, it is important that the meaning and the steps of a technique are understood before its application, and its assumptions (e.g. normal distribution) are known and respected. A cooperation between chemometricians, analytical chemists and expert in the investigated matrices would be very useful in order to apply the techniques correctly as well as to obtain as much information as possible from the experimental results.

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Captions to figures

Fig. 1. Combined plot of scores and loadings obtained by PCA for pH and element percentages extracted from contaminated soil samples (coded A1-A31) into the third fraction of Tessier's procedure, after column standardization [80].

Fig. 2. Loadings from PC2 based on LOI-normalized data (all fractions) for roadside soil samples versus the leachable fraction (averages for all 16 samples calculated on a dry weight basis) for all elements. Correlation coefficient, $r^2 = 0.76$ (from [50] by permission of Springer).

Fig. 3. Loading plots obtained with Multy-way PCA applied to the results of the BCR scheme for marine sediments. (a) A-mode; (b) B-mode; (c) C-mode (from [136] by permission of Elsevier).

Table 1

Sequential extraction procedures adopted in the papers cited in this review.

| Procedure | Comment | Ref. |
|---|--|---------------------------|
| Tessier's sequential extraction: exchangeable (1 M MgCl ₂ , pH 7); bound to carbonates (1 M CH ₃ COONa/ CH ₃ COOH, pH 5); bound to Fe-Mn oxides (0.04 M NH ₂ OH·HCl in 25% v/v CH ₃ COOH, 96°C); bound to organic matter (HNO ₃ /H ₂ O ₂ , pH 2, 85°C; 3.2 M CH ₃ COONH ₄ in 20% v/v HNO ₃); residual (HF/HClO ₄). The original reference reports also the possibility to use 1 M CH ₃ COONa, pH 8.2 and 0.3 M Na ₂ S ₂ O ₄ /0.175 M Na-citrate/0.025 M H-citrate for the first and third fractions respectively. | One of the first sequential extraction procedures developed. Most of the other procedures derive from it. It was the most extensively applied scheme before the introduction of the BCR protocol. | [44,49,80, 88,95,116,131] |
| Revised BCR sequential extraction: exchangeable, water- and acid-soluble (0.11 M CH ₃ COOH); reducible (0.5 M NH ₄ OH·HCl, pH 1.5); oxidisable (H ₂ O ₂ ; 1 M CH ₃ COONH ₄ , pH 2); residual, recommended (aqua regia). | Developed by SMT in order to harmonize fractionation procedures and ensure comparability. It provides a detailed description of operative conditions. For these characteristics it is the most extensively applied sequential extraction technique nowadays. | [33-44,130,136] |
| Modified Tessier's sequential extraction: exchangeable (1 M CH ₃ COONH ₄ , pH 7); carbonate-bound (1 M CH ₃ COONa/ CH ₃ COOH, pH 5); bound to Fe-Mn oxides (0.04 M NH ₂ OH·HCl in 25% v/v CH ₃ COOH, 96°C); bound to organic matter (HNO ₃ /H ₂ O ₂ , pH 2, 85°C; 3.2 M CH ₃ COONH ₄ in 20% v/v HNO ₃); lithogenic (aqua regia/HF). | Based on Tessier's scheme. The differences are: exchangeable fraction following Kersten and Förstner's scheme [32]; reagents for lithogenic fraction. | [49,54] |
| 5-step sequential extraction: exchangeable (1 M CH ₃ COONH ₄ , pH 7); bound to carbonates (1 M CH ₃ COONa/ CH ₃ COOH, pH 5); bound to Mn oxides (0.1M NH ₂ OH·HCl in 0.1M HNO ₃); bound to Fe-oxides (0.04 M NH ₂ OH·HCl in 25% v/v CH ₃ COOH, 96°C); bound to organic matter (0.1 M HNO ₃ /H ₂ O ₂ , 85°C; 3.2 M CH ₃ COONH ₄ in 20% v/v HNO ₃). | Based on Tessier's scheme. The differences are: distinction between Mn and Fe oxides; exchangeable fraction following Kersten and Förstner's scheme [32]; absence of the residual fraction. | [46,47,48] |
| 5-step sequential extraction: exchangeable (1 M CH ₃ COONH ₄ , pH 7); bound to carbonates and easily reducible phases (0.6 M HCl, pH 4; 0.1 M NH ₂ OH·HCl in 0.01 M HCl, pH 2); bound to moderately reducible phases (0.2 M (NH ₄) ₂ C ₂ O ₄ /0.2 M H ₂ C ₂ O ₄ , pH 3); bound to organic matter and sulphides (HNO ₃ /H ₂ O ₂ , pH 2, 85°C; 3.2 M CH ₃ COONH ₄); bound to acid-soluble residue (6 M HCl, 85°C). | Uncommon fractionation pattern; elements nominally bound to carbonates and easily reducible phases extracted in the same step; most reagents are different from Tessier's scheme. | [52] |

Table 1 (continued)

| Procedure | Comment | Ref. |
|---|---|------|
| 5-step sequential extraction: exchangeable (1 M CH ₃ COONH ₄ , pH 7); bound to carbonates and easily reducible phases (0.6 M HCl, pH 4; 0.1 M NH ₂ OH·HCl in 0.01 M HCl, pH 2); bound to moderately reducible phases (0.2 M (NH ₄) ₂ C ₂ O ₄ /0.2 M H ₂ C ₂ O ₄ , pH 3); bound to organic matter and sulphides (HNO ₃ /H ₂ O ₂ , pH 2, 85°C; 3.2 M CH ₃ COONH ₄); bound to acid-soluble residue (6 M HCl, 85°C). | Uncommon fractionation pattern; elements nominally bound to carbonates and easily reducible phases extracted in the same step; most reagents are different from Tessier's scheme. | [52] |
| Scheme 1: exchangeable and soluble in water and acids (0.11 M CH ₃ COOH); reducible (0.1 M NH ₂ H·HCl/HNO ₃ , pH 2); oxidisable (8.8 M H ₂ O ₂ /HNO ₃ , pH 2; 3.2 M CH ₃ COONH ₄ /HNO ₃ , pH 2); residual (HF/HCl/HNO ₃ ; HClO ₄ ; HNO ₃). Scheme 2: exchangeable and associated to carbonates (1 M MgCl ₂ , pH 7; 1 M CH ₃ COONa/CH ₃ COOH, pH 5); associated to oxides of Fe and Mn (0.04 M NH ₂ OH·HCl in 25% v/v CH ₃ COOH); associated to organic matter and sulfides (HNO ₃ /H ₂ O ₂ , pH 2; 3.2 M CH ₃ COONH ₄); residual (HClO ₄ /HF; HCl). Scheme 3: soluble, exchangeable and associated to carbonates (H ₂ O; 1 M CH ₃ COONH ₄ ; 1 M CH ₃ COONa, pH 5); associated to oxides of Fe and Mn (0.04 M NH ₂ OH·HCl in 25% v/v CH ₃ COOH/HNO ₃ , pH 2; 1 M HNO ₃); associated to organic matter and sulfides (HNO ₃ /H ₂ O ₂ , pH 2; 0.3 M CH ₃ COONH ₄); residual (HClO ₄ /HNO ₃). | Scheme 1: steps 1-3 according to the original BCR scheme, except for the concentration of CH ₃ COONH ₄ . Scheme 2: based on Tessier's scheme. The difference is the summing up of the first two fractions. Scheme 3: based on Tessiers's scheme. The differences are: presence of a step for water-soluble elements; exchangeable fraction following Kersten and Förstner's scheme [32]; summing up of the first three steps. | [40] |
| 4-step sequential extraction: exchangeable and acid-soluble (1 M CH ₃ COONa, pH 5); reducible (0.04 M NH ₂ OH·HCl in 25% v/v CH ₃ COOH); oxidisable (HNO ₃ /H ₂ O ₂ , pH 2, 85°C; cooling; 3.2 M CH ₃ COONH ₄ in 20% v/v HNO ₃); residual (HNO ₃ /H ₂ O). | Based on BCR scheme. The difference is in the exchangeable fraction, following Kersten and Förstner's scheme [32]. | [50] |
| 4-step sequential extraction: soluble and exchangeable (H ₂ O); carbonates, oxides and reducible (0.25 M NH ₂ OH·HCl, pH 2); bound to organic matter, oxidable and sulphidic (H ₂ O ₂ twice; 2.5 M CH ₃ COONH ₄); residual (HNO ₃ /HCl/HF/HClO ₄ /H ₂ O ₂). | Uncommon fractionation pattern; soluble and exchangeable elements extracted in the same step; elements nominally bound to carbonates oxides and reducible phases extracted in the same step. | [45] |

Table 1 (continued)

| Procedure | Comment | Ref. |
|---|---|------|
| 2-step sequential extraction: mobile (0.01 M CaCl_2); mobilisable (0.005 M DTPA). | Short procedure. Proposed as an alternative to Tessier's scheme for the measurement of the labile element portion . | [94] |
| 6-step sequential extraction: labile inorganic and labile organic (0.5 M NaHCO_3); inorganic moderately labile, chemisorbed on Fe, Al and organic moderately labile, chemisorbed on humic acids (0.1 M NaOH); within small stable aggregates, physically inaccessible and within small stable aggregates, physically inaccessible (0.1 M NaOH + sonication); Ca-bound (1 M HCl); residual inorganic (HCl); residual organic (HCl/ H_2O_2). | Sequential extraction scheme for P. It is distinctly different from procedures for metals, owing to the anionic nature of P compounds. | [53] |
| 5-step sequential extraction: exchangeable (1 M $\text{Mg}(\text{NO}_3)_2$); organically bound or associated with organic matter (0.7 M NaOCl); in crystalline Mn oxide or coprecipitated (0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}/\text{H}_2\text{C}_2\text{O}_4$); in crystalline Fe oxide or coprecipitated ($\text{Na}_2\text{S}_2\text{O}_4$). | Sequential extraction scheme for Fe, Mn and Al. The reagents and the operational definitions of the fractions substantially differ from the popular Tessier's and BCR schemes. | |
| 4-step sequential extraction: loosely sorbed (1 M NH_4Cl); reductant soluble (0.11 M $\text{NaHCO}_3/\text{Na}_2\text{S}_2\text{O}_4$); metal oxide bound (1 M NaOH); calcium bound (0.5 M HCl). | Sequential extraction scheme for P. It differs from the scheme for P cited above for the nature and/or concentrations of the reagents and for the definitions of the fractions. | [56] |
| 4-step sequential extraction: soil solution and labile (water and anion exchange resin); labile, inorganic, organic and microbic (0.5 M NaHCO_3 , pH 8.2); in humic and fulvic acids and in Al and Fe phosphates (0.1 M NaOH); hardly soluble (1 M H_2SO_4). | Sequential extraction scheme for P. Characterized by the use of an anion exchange resin in addition to chemicals. | [57] |
| 4-step sequential extraction : plant-available and water-extractable (H_2O); weakly sorbed-bioavailable organic and inorganic (0.5 M NaHCO_3 , pH 8.2); strongly bound chemisorbed-potentially bioavailable (0.1 M NaOH); apatite or Ca-bound and non-bioavailable (1 M HCl). | Sequential extraction scheme for P. The reagents are similar to the ones reported in the previously mentioned schemes, but the definitions of the fractions are different. | [58] |

Table 1 (continued)

| Procedure | Comment | Ref. |
|---|---|---------|
| 6-step sequential extraction: organomercury (CHCl_3 ; 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$); water-soluble (H_2O); acid-soluble (0.5 M HCl); associated to humic matter (0.2 M NaOH); elemental (aqua regia, 150°C); residual, HgS (aqua regia). | Sequential extraction scheme for Hg. The reagents and the operational definitions of the fractions substantially differ from the popular Tessier's and BCR schemes. | [55] |
| 3-step sequential extraction: exchangeable (1 M $\text{CH}_3\text{COONH}_4$); readily soluble nonexchangeable (0.01 M HCl); recalcitrant nonexchangeable (0.2 M sodium tetraphenylborate). | Sequential extraction scheme for K. It is mainly focused on the exchangeability of the element. | [118] |
| Physiologically Based Extraction Test (PBET): simulated stomach conditions (simulated stomach fluid: 1.25 g pepsin, 0.50 g sodium malate, 0.50 g sodium citrate, 420 μL lactic acid and 500 μL acetic acid made up to 1 L with $\text{H}_2\text{O}/\text{HCl}$, pH 2.5, 37°C); simulated small intestine conditions (pH 7 with NaHCO_3 , addition of bile salts and pancreatine to the simulated stomach fluid). | Aimed at studying element bioaccessibility. It simulates gastrointestinal tract environment. | [66,69] |
| Modified PBET: stomach phase (simulated stomach fluid: 1.25 g pepsin, 0.50 g sodium malate, 0.50 g sodium citrate, 420 μL lactic acid and 500 μL acetic acid made up to 1 L with $\text{H}_2\text{O}/\text{HCl}$, pH 2.5, 37°C); small intestine 1 (pH 7 with NaHCO_3 , addition of 175 mg bile salts and 50 mg pancreatine to the simulated stomach fluid); small intestine 2 (the same as small intestine 1 after an additional 2 hours incubation). | Aimed at studying element bioaccessibility. It differs from the above cited PBET method for the presence of two steps in simulated intestine conditions. | [68] |
| Simplified PBET (SBET): 30.03 g L^{-1} glycine/ HCl , pH 1.5, 37°C . | Aimed at studying element bioaccessibility. It considers only one gastric phase. | [67] |

Table 2

Selected applications of chemometric techniques to single or sequential extraction results. The papers are arranged in the order in which they were cited in sections 4.1, 4.2 and 5.

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|---|------------------------------------|--|--|---------------------------------------|----------------|----------|
| Surface river sediments (Louros River, Greece) | P | UV-vis spectrophotometry | 4-step sequential extraction, speciation within each extract | ANOVA, PCA, HCA, LDA | SPSS 13.0 | [58] |
| Lake sediments (Volvi and Koronia Lakes, Greece) | Al, Ca, Fe, Mg, Mn, P | FAAS, GF-AAS, UV-vis spectrophotometry | Single extraction (Al, Ca, Fe, Mg, Mn; 1 M CH ₃ COONH ₄); P: 4-step sequential extraction | ANOVA, PCA | SPSS 8.0S | [56] |
| Contaminated soil treated with organic residues (Aljustrel mining area, Portugal) | Cu, Pb, Zn | FAAS, GF-AAS | Single extractions (0.01 M CaCl ₂ pH 5.7, 0.5 M CH ₃ COO NH ₄ , 0.5 M CH ₃ COOH, 0.02 M EDTA), BCR | ANOVA, Correlation analysis, PCA, HCA | Statistica 6.0 | [37] |
| Contaminated soils (along Dommel River, the Netherlands) | Cd, Fe, Ni, Zn | FAAS | Single extraction (0.01 M CaCl ₂) | ANOVA, PCA | Canoco 4.5 | [129112] |
| Muddy and sandy marine sediments (Egyptian coast, Mediterranean Sea) | Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn | FAAS | Single extraction (6 M HCl) | Correlation analysis, PCA | SPSS 10.0 | [22] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|---|--|----------------------|---|--|----------------------|-------|
| Forest soils (Kitsatchie National Forest, Winn Parish, Louisiana) | Ca, Mg, K, Fe, Mn | ICP-AES | Single extraction (Mehlich III extractant: 0.2 M CH ₃ COOH, 0.25 M NH ₄ NO ₃ , 0.015 M NH ₄ F, 0.013M HNO ₃ , 0.001M EDTA) | Correlation analysis, geostatistics | GS ⁺ | [102] |
| Soils from a national database project (Ireland) | K, Mg, P (plus total Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, Hg, La, Li, Mg, Mn, Mo, Na, Nb, Ni Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Y, Zn) | ICP-AES, ICP-MS | Single extraction (acetate buffer) | Correlation analysis, HCA | SPSS 14 | [107] |
| Roadside sediments (Seoul, Korea) | As, Cd, Cr, Cu, Pb, Zn | ICP-AES, HG-AAS | Single extraction (0.1 M HCl) | Correlation analysis, FA | Not reported | [111] |
| Forest soils (La Coruña, Spain) | Co, Cr, Fe, Mn, Ni, Zn | ICP-MS | Single extraction (0.05 M EDTA) | Correlation analysis, geostatistics | KRIGE, COKRI, Surfer | [114] |
| Soil from an experimental area (Volperino, Italy) | Fe, Mn | ICP-AES | Single extraction (Fe and Mn:0.005 M DTPA/0.01 M CaCl/ 0.1 M tetraethylammonium | Correlation analysis, geostatistics, FKA | Not reported | [113] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|--|----------------------------|----------------------|---|--------------------------------|-----------------------|-------|
| Soils with different composition and pollution levels (Flanders, Belgium) | Cd | ICP-AES, GF-AAS | Soil solution, single extractions (0.01 M CaCl_2 , 0.1 M $\text{Ca}(\text{NO}_3)_2$, 0.1 M NaNO_3 , 1 M NH_4NO_3 , 1M CH_3CONH_4 , 1 M MgCl_2 , 0.11 M CH_3COOH , 0.1 M HCl , 0.5M HNO_3 , 0.02 M EDTA +0.5 M $\text{CH}_3\text{COONH}_4$ +0.5 M CH_3COOH pH 4.65, 0.005 M DTPA +0.01 M CaCl_2 +0.1 M TEA pH 7.3, aqua regia) | Correlation analysis, HCA, MLR | SPSS 11.0 | [115] |
| Urban and olive oil sludge (Ourense town and province of Jaén, Spain) | Cr, Cu, Ni, Pb, Zn | FAAS | Single microwave extractions (with BCR extractants), BCR, | Correlation analysis, PCA | Statistica | [39] |
| River sediments (Ell-Ren River, Southern Taiwan) | Cd, Co, Cr, Cu, Ni, Pb, Zn | Not reported | 5-step-sequential extraction | Correlation analysis, PCA | Not reported | [48] |
| River sediments (Haihe River, China) | Cd, Cu, Co, Ni, Mn, Pb | GF-AAS | Tessier | Correlation analysis, PCA | SPSS 12.0 for Windows | [116] |
| River sediments (Yenshui, Tsengwen, Chishui, Potzu, Peikang rivers, southern Taiwan) | Co, Cr, Cu, Ni, Pb, Zn, | AAS | 5-step sequential extraction | Correlation analysis, PCA | Not reported | [47] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|--|------------------------------------|----------------------|---|-------------------------------------|----------------------|-------|
| Alluvial river sediments (Danube river, Pančevo Oil Refinery, Serbia) | Cu, Fe, Mn, Ni, Pb, Zn, | FAAS | 5-step sequential extraction | Correlation analysis, PCA, HCA | SPSS for Windows 10 | [52] |
| Soil from a landfill (Bedfordshire,UK) | Cr, Cu, Zn | ICP-AES | Tessier | Correlation analysis, geostatistics | VARIOWIN 2.2 | [95] |
| Uncontaminated soils (Central Spain) | Mn, Zn | AAS | Single extraction (0.05 M EDTA), modified Tessier, BCR, | Correlation analysis, MLR | Statgraphic Plus 5.0 | [44] |
| Soil affected by the Aznancóllar mine spill (Spain) | As, Cd, Cu, Pb, Zn | Not reported | Single extraction (0.05 M EDTA) | Correlation analysis, geostatistics | VESPER 1.6 | [104] |
| Surface soils from seven land uses. (Fuyang County, China) | Cu | AAS | Single extraction (DTPA, CaCl ₂ , TEA) | Correlation analysis, geostatistics | SPSS 10.0 | [110] |
| Agricultural soils with vegetable crops (Lower Vinalopò region, Spain) | Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn | FAAS, GF-AAS | Single extraction (0.05 M EDTA, pH 7) | Correlation analysis, HCA | SPSS 13.0 | [120] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|---|--|----------------------|--|-------------------------------------|-----------------------------------|-------|
| Agricultural cambisol (Kassow, Germany) | P | Colorimetry | Single extractions (0.01 M CaCl ₂ , 0.5 M CH ₃ COONH ₄ /0.5 M CH ₃ COOH/0.02 M Na ₂ -EDTA; 0.43 M HNO ₃ ; aqua regia; 0.1M Ca-lactate/0.1 M Ca-acetate/ 0.3M CH ₃ COOH) | Correlation analysis, geostatistics | Variowin 2.2 | [117] |
| Soils from rice fields (Takatsuki City, Japan) | K, N, P | FES, colorimetry | 3-step sequential extraction (K), water and Bray method (P), single extractions (N: 2 M KCl) | Correlation analysis, geostatistics | GS ⁺ | [118] |
| Contaminated and uncontaminated soils and sediments (Flanders, Belgium) | Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn | ICP-AES, FES | Soil solution | Correlation analysis, MLR | SPSS 10.0, Excel 9.0, Surfer 6.04 | [119] |
| Contaminated soils from an abandoned mining area (Salsigne, France) | As, Cd, Cu, Ni, Pb, Zn | ICP-AES, ICP-MS | BCR | Correlation analysis, PCA, HCA | SPSS 10.0, XI-Stat 5.2 | [35] |
| Roadside soil and dust (Sweden) | Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Rb, Sr, U, V, W, Zn | ICP-MS | 4-step sequential extraction | Correlation analysis, PCA | The Unscrambler 7.01 | [50] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|--|--|----------------------|--|-------------------------------------|-----------------|-------|
| Agricultural soils irrigated with wastewater (Hidalgo State, Mexico) | B, Ca, Cd, Cr, K, Mg, Na, Pb | ICP-AES | Extraction with water followed by Tessier | Correlation analysis, PCA | SPSS 10 | [51] |
| River sediments and floodplain soil (Warta River, Poland) | Hg | CV-AFS | 6-step sequential extraction for Hg | Correlation analysis, ANN | Statistica 6.0 | [55] |
| Agricultural soils (Harz mountains, northeastern Germany) | K, Mg, P | ICP-AES | 4-step sequential extraction (P), double lactate extraction (K, Mg, P) | Correlation analysis, geostatistics | Surfer | [57] |
| Soil profiles (Torun, Poland) | Cd, Ni, Pb | FAAS | Column leaching with modeled acid rain | Correlation analysis, ANN | Statistica 6-0 | [82] |
| Calcaric Fluvisols (Spain) | Ca, K, Mg, Na, Si (+ anions) | FAAS, FAES | Column leaching with water | Correlation analysis, RDA | Canoco 4.5 | [83] |
| 587 soils (North Dakota) | Zn | AAS | DTPA | Correlation analysis, geostatistics | GSLIB | [91] |
| Lake sediments (The Netherlands) | Al, Ca, Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, S, Zn | ICP-AES, ICP-MS | Single extraction (1 M HCl, expressed as SEM, see text) | Correlation analysis, geostatistics | WLSFIT, Surfer | [98] |
| Forest soil (northwestern Spain) | N, P | Colorimetry | Single extraction (1 M) | Correlation analysis, geostatistics | R 1.8 for Linux | [105] |
| Agricultural soils (central Greece) | Cd, N | GF-AAS | Single extractions (Cd: DTPA) | Correlation analysis, geostatistics | GIS | [108] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|--|------------------------------------|----------------------|--|--|--------------------------|-------|
| Agricultural soils (northeast China) | K, N, P | Colorimetry | Single extractions (K: 1 M CH ₃ COONH ₄) | Correlation analysis, geostatistics | GS ⁺ , GIS | [123] |
| Agricultural soils from an experimental area (Italy) | K, Na, P | Not reported | Single extractions (K, Na: CH ₃ COONH ₄ ; P: NaHCO ₃); | Correlation analysis, geostatistics, FKA | Not reported | [121] |
| Forest soil (North Carolina) | Al, Fe, P | Not reported | Single extraction (Al, Fe: oxalate) | Correlation analysis, geostatistics | GS ⁺ | [122] |
| Agricultural soils (northeast China) | K, N, P | Colorimetry | Single extractions (K: 1M CH ₃ COONH ₄) | Correlation analysis, geostatistics | GS ⁺ , ArcGIS | [124] |
| Soils from urban garden (Kayseri, Turkey) | Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn | FAAS | BCR | Correlation analysis, PCA, HCA | SPSS 9.05 | [33] |
| Forest soils (northwestern Spain) | N, P | Colorimetry | Single extraction (N: 2 M KCl; P: 2.5 % CH ₃ COOH) | Correlation analysis, geostatistics | R | [100] |
| Agricultural soils (South Australia) | Cd | GF-AAS | Single extractions (0.01 and 0.05 M CaCl ₂ , 0.1 M Na ₂ EDTA, 0.005 M DTPA-TEA, 1 M NH ₄ NO ₃ , 0.02 M AAAC-EDTA, 1 M NH ₄ Cl | Correlation analysis, MLR | Not reported | [126] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|--|--|----------------------|---|-------------------------------------|----------------------------------|-------|
| Soils from around a zinc smelter (Kayseri, Turkey) and grapes | Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn | FAAS | Single extractions (0.1M HCl in 0.025 M H ₂ SO ₄ , 1 M CH ₃ COONH ₄ , aqua regia) | Correlation analysis, PCA, HCA | SPSS 10.0 | [125] |
| Forest soils (Jizera Mountains, Bohemia, Czech Republic) | Al | ICP-AES | Single extraction (0.5 M KCl, 0.05M Na ₄ P ₂ O ₇) | Correlation analysis, geostatistics | GS ⁺ , VARIO WIN 2.21 | [127] |
| Surficial river sediments (Louro River, Galicia, Spain) | Cd, Cr, Cu, Ni, Pb | GF-AAS | BCR | PCA | StatView for Apple Macintosh | [34] |
| River sediments (Yenshui, Tsengwen, Chishui, Potzu, Peikang rivers, southern Taiwan) | Co, Cr, Cu, Ni, Pb, Zn | Not reported | Modified Tessier's procedure | PCA | Not reported | [46] |
| Marine sediments (Terra Nova Bay, Antarctica) | Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn | ICP-AES, GF-AAS | BCR | PCA, HCA | XLSTAT | [38] |
| Estuarine sediments affected by the Aznancóllar mine spill (Guadamar and Guadalquivir rivers, Spain) | Cd, Cu, Fe, Mn, Pb, Zn | DPASV, FAAS | Modified Tessier's scheme | PCA | BMDP | [49] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|---|--|----------------------|--|-----------------------|--------------|-------|
| Mangrove sediments (Mengkabong Lagoon, Sabah, Malaysia) | Al, Ca, Cu, Fe, K, Na, Mg, Pb, Zn | FAAS | Single extraction (Na, K, Ca, Mg: CH ₃ COONH ₄ ; other elements: aqua regia) | PCA, HCA | Not reported | [129] |
| Agricultural soils (Piedmont, Italy) | Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Ti, Zn | ICP-AES, GF-AAS | Single extraction (0.02 M EDTA in 0.5 M CH ₃ COONH ₄), Tessier | PCA, HCA | XLSTAT | [88] |
| Contaminated soils (Piedmont, Italy) | Al, Cu, Cr, Fe, La, Mn, Ni, Pb, Sc, Ti, V, Y, Zn | ICP-AES | Tessier | PCA, HCA | XLSTAT | [80] |
| Contaminated soils (Piedmont, Italy) | Al, Cd, Cu, Cr, Fe, La, Mn, Ni, Pb, Sc, Ti, V, Y, Zn, Zr | ICP-AES, GF-AAS | Single extractions (water, 0.5 M CH ₃ COOH, 0.02 M EDTA in 0.5 M CH ₃ COONH ₄) | PCA, HCA | XLSTAT | [89] |
| Superficial soil and grass (Gipuzkoa, Spain). | Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn | GF-AAS | 2-step sequential extraction | PCA | Statistica | [94] |
| Urban soils (Sevilla, Spain; Torino, Italy; Glasglow, UK) | Cr, Cu, Fe, Mn, Ni, Pb, Zn | Not reported | Single extractions (0.05 M EDTA, 0.5 M HCl, aqua regia), BCR | PCA | SPSS 11.5.1 | [36] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|--|---|----------------------|--|-------------------------------|---------------------------------------|-------|
| Dust in schools (Caracas, Venezuela) | Cd, Cr, Cu, Mn, Ni, Pb, V, Zn | ICP-AES | 4-step sequential extraction | PCA | Multi-Variate Statistical Package 3.1 | [45] |
| Ferrite precipitated from polluted effluents | Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn | ICP-AES | BCR | PCA, HCA | Minitab 10X | [130] |
| River sediments (Pisuerga and Carrión rivers, Spain) | Cd, Co, Cu, Ni, Pb, Zn | DPAdCSV, DPASV | Tessier | Correlation analysis, PCA | Not reported | [131] |
| Mine-impacted river sediments (Cacalotenango and Taxco rivers, Mexico) | Pb | Not reported | Modified Tessier extraction | FA | Not reported | [54] |
| Gold tailing dumps materials (Witwaterands, South Africa) | Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Zn, | XRF, ICP-AES | Column leaching with natural and acidified rainwater | FA | Statistica | [81] |
| Alfisols, Ultisols, Oxisols soils (Misiones Province, Argentina) | Al, Ca, Fe, Mg, Mn, P | Not reported | P: 11-step fractionation; Al, Fe, Mn: 5-step sequential extraction; single extractions (Al: KCl; Ca and Mg: CH ₃ COONH ₄) | FA, LDA | Not reported | [53] |
| Acidic forest soils (Tyrol, Austria) | Al | AAS | 1 M HCl | Correlation analysis, FA, MLR | Not reported | [97] |

Table 2 (continued)

| Matrix | Elements | Analytical technique | Extraction procedure | Chemometric treatment | Software | Ref. |
|---|---|----------------------|---|---|----------------------------|-------|
| Soil collected around a coal-fuelled power plant (Velilla del Río Carrión, Spain) | As, Cd, Co, Cr, Cu, Ni, Pb, Zn | ICP-AES, GF-AAS | BCR | PCA, MA, PARAFAC, TUCKER3 N-way methods | Minitab 13.0, Matlab 6 | [41] |
| Marine sediments (Mejillones del Sur bay, Chile) | Al, As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, V, Zn | ICP-AES, GF-AAS | BCR | MA, PARAFAC, N-way method | Minitab 13.0, Matlab 6 | [136] |
| Estuarine sediments (Bahía Blanca, Buenos Aires, Argentina) | Cd, Cr, Cu, Pb, Zn | ICP-AES | Scheme 1, Scheme 2; Scheme 3 | PARAFAC N-way method | Matlab 7.0 | [40] |
| Contaminated soil profiles (Bad Liebenstein, Thuringia, Germany) | Cd, Co, Cr, Cu, Eu, Fe, Mn, Ni, Pb, Sb, Se, Y, Zn | ICP-AES, ICP-MS | BCR | Tucker3 N-way method | Not reported | [42] |
| Soils irrigated with wastewater (Jajmau area, India) | Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Zn | AAS | Single extractions (water; Na, K, Ca, Mg: 1.0 M NH ₄ Cl; P: 0.5 M NaHCO ₃) | 2-way PCA + unfolding, PARAFAC, TUCKER3 N-way methods | Statistica 7.0; Matlab 7.0 | [133] |

List of abbreviations. AAS: atomic absorption spectroscopy (the atomizer was not indicated); ANN: Artificial Neural Network; CV-AFS Cold Vapour Atomic Fluorescence Spectroscopy; DGT: Diffusive Gradients in Thin Films; DPAdCSV: Differential Pulse Adsorptive Cathodic Stripping Voltammetry; DPASV: Differential Pulse Anodic Stripping Voltammetry; FAAS: Flame Atomic Absorption Spectroscopy; FES: Flame Emission Spectroscopy; FKA: Factorial Kriging Analysis; GF-AAS: Graphite Furnace Atomic Absorption Spectroscopy; HG-AAS: Hydride Generation Atomic Absorption Spectroscopy; IC: Ion Chromatography; ICP-AES: Inductively Coupled Plasma Atomic Emission Spectroscopy; ICP-MS: Inductively Coupled Plasma Mass Spectrometry; LDA = Linear Discriminant Analysis; MLR = Multiple Linear Regression; RDA: Redundancy Analysis; XRF: X Ray Fluorescence.

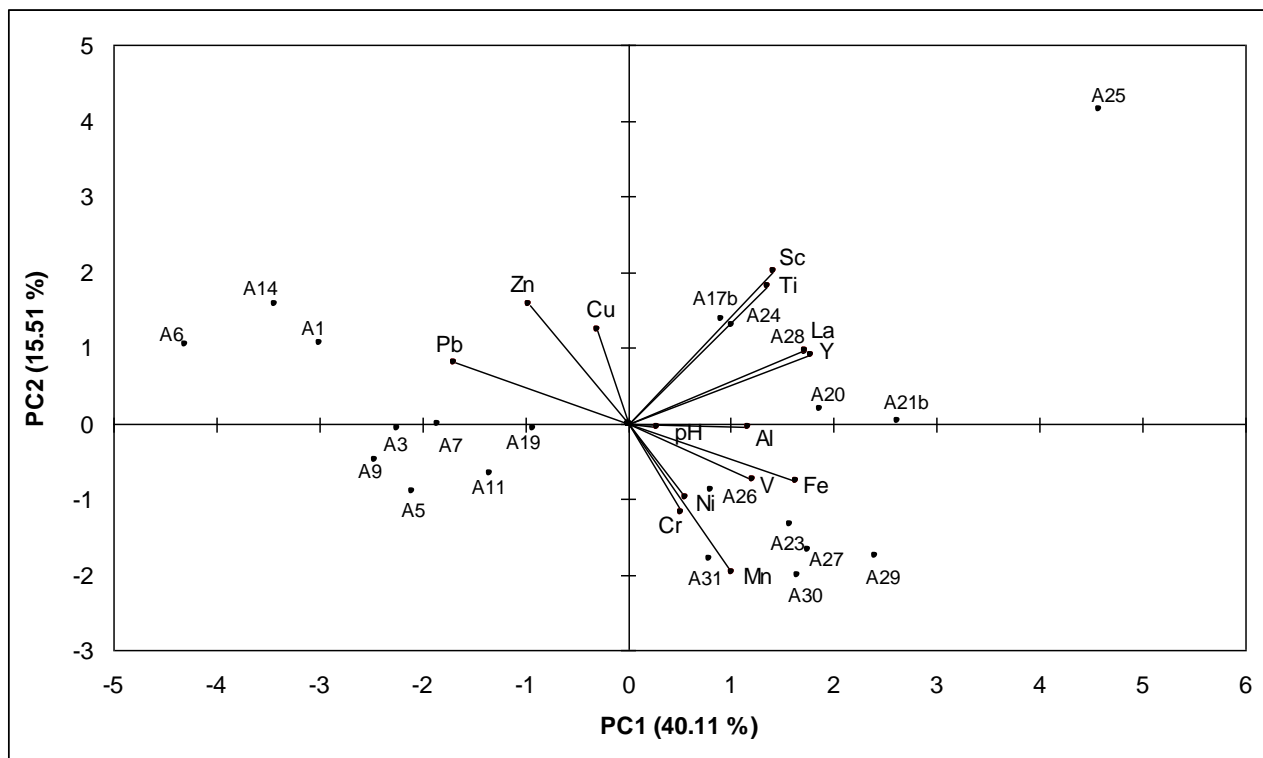


Fig. 1

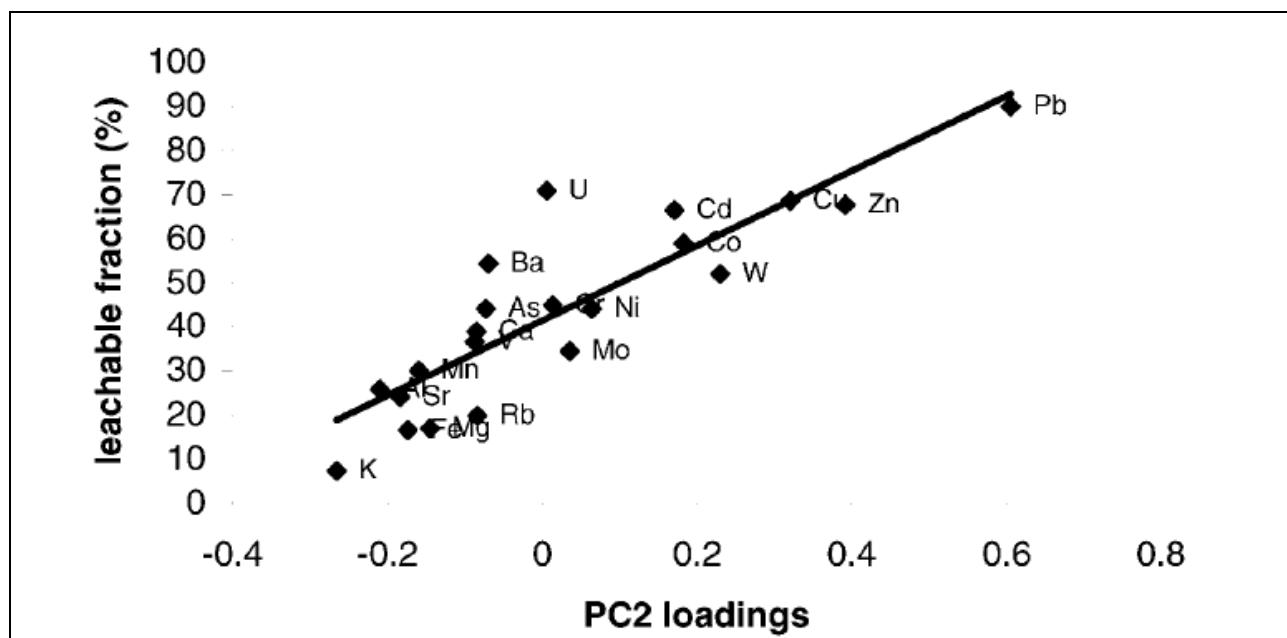


Fig. 2

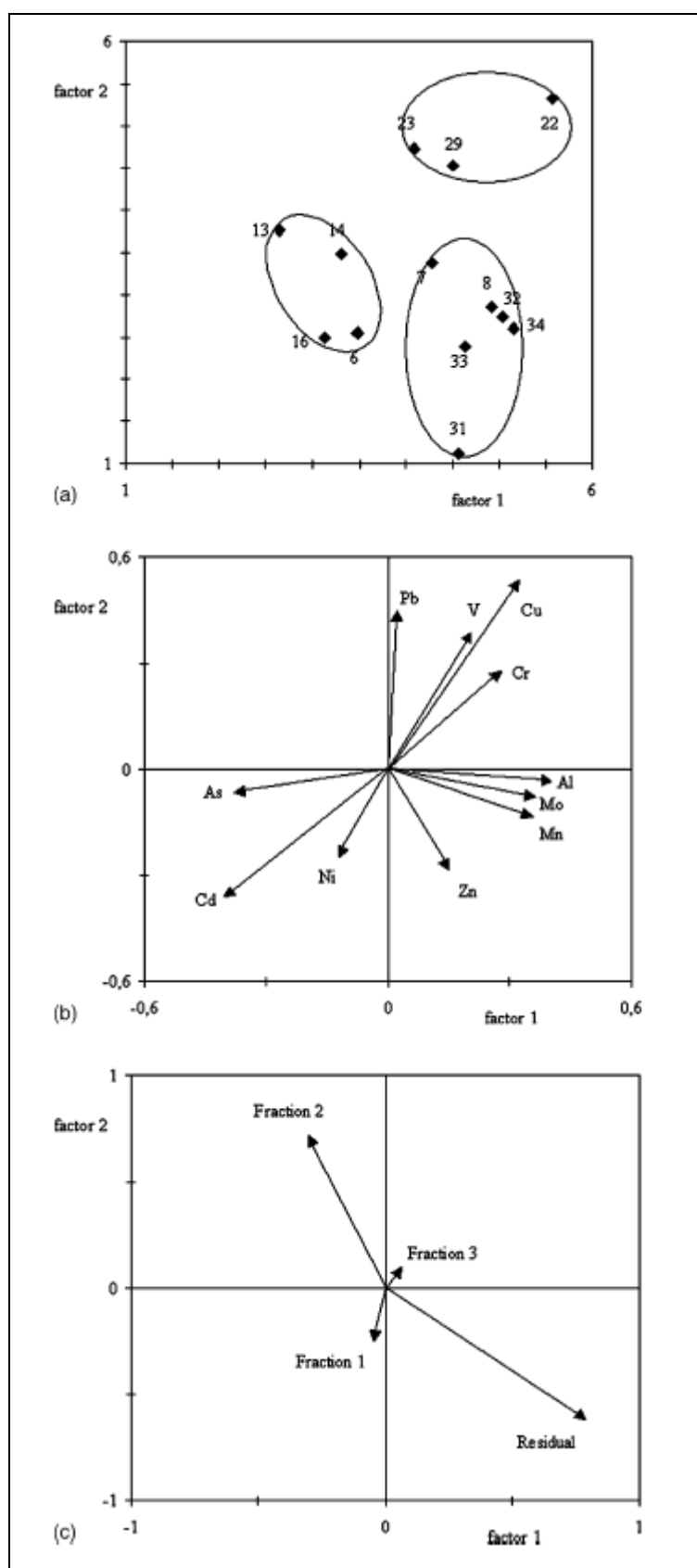


Fig. 3



Ornella Abollino received her PhD in Chemical Sciences in 1991 from the University of Torino. She is presently Associate Professor of Analytical Chemistry at the Faculty of Pharmacy, University of Torino. Her research activities are mainly focused on the following topics: development of voltammetric and spectroscopic procedures for the determination and speciation of trace metals; study of element fractionation in sediment and soils from remote and anthropized areas; characterization of metal content in pharmaceutical formulations; interaction between trace metals and plants; application of chemometric techniques for the processing of experimental results related to the above mentioned matrices.



Mery Malandrino received her PhD in Chemical Sciences in 2001 at the University of Torino. She is presently Researcher of Analytical Chemistry at the Faculty of Sciences of the University of Torino. She is mainly involved in the development of sensitive analytical procedures capable of characterising complex environmental matrices, such as soils, sediments and atmospheric particulate matter. She uses chemometrics to interpret experimental results. The purpose of her studies is to gain insight into the behaviour of elements in uncontaminated ecosystems and their influence on climate changes. Furthermore, she studies the development of eco-compatible decontamination procedures for polluted soils.



Agnese Giacomino graduated in Chemistry in 2003 at the University of Torino. She received her PhD in Chemical Sciences in 2007 at the University of Torino. Now she is holder of a research grant at the Department of Analytical Chemistry of the University of Torino. Her research activities are finalized to study the behaviour of metals in different natural matrices (soils, sediments, vegetables, seawater...), using chemometrics for data processing, to characterize the composition of pharmaceutical formulations, to develop new procedures of remediation of contaminated soils, to study analytical methods for the determination of trace metals.



Edoardo Mentasti has been full professor of Analytical Chemistry at the Faculty of Sciences of the University of Torino from 1980 to 2007 and is now retired. He has been Editor-in-chief of the Journal *Annali di Chimica* from 1996 to 2006. His main research interests are the development of preconcentration and speciation procedures for trace metal ions coupled to determination by atomic spectroscopy, the development of voltammetric methods of analysis, the characterization of environmental compartments (seawaters, lacustrine ecosystems, sediments, soils) with the aid of chemometric techniques, the interaction between trace metals and clays, the remediation of contaminated soils.